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[Title of the Invention]

AQUEOUS EMULSION AND ADHESIVE FOR WOODWORK

[Abstract]

[Problem]

To obtain an aqueous emulsion having high viscosity, good water resistance and good adhesiveness to wood, and to obtain an adhesive for woodwork.

[Means for Solution]

An aqueous emulsion which comprises, as the dispersoid, a polymer having vinyl ester monomer units, and, as the dispersant, a composition comprising a vinyl alcohol polymer (A) having an ethylene unit content of from 0.5 to 10 mol% and a degree of saponification (X) of at least 95 mol%, and a vinyl alcohol polymer (B) having a degree of saponification (Y) of from 75 to 95 mol%, and satisfying $X - Y \geq 0.5$ mol%; and an adhesive for wood that comprises the above emulsion.

[Claims]

[Claim 1]

An aqueous emulsion which comprises, as the dispersoid, a polymer having vinyl ester monomer units, and, as the dispersant, a composition comprising a vinyl alcohol polymer (A) having an ethylene unit content of from 0.5 to 10 mol% and a degree of saponification (X) of at least 95 mol%, and a vinyl alcohol polymer (B) having a degree of saponification (Y) of from 75 to 95 mol%, and satisfying $X - Y \geq 0.5$ mol%.

[Claim 2]

The aqueous emulsion as claimed in claim 1, wherein the ratio of the vinyl alcohol polymer (A) to (B) falls between 9.9/0.1 and 5/5.

[Claim 3]

The aqueous emulsion as claimed in claim 1 or 2, wherein the dispersoid is a polymer comprising vinyl ester monomer and ethylene units.

[Claim 4]

An adhesive for wood, comprising the aqueous emulsion of claims 1 to 3.

[Detailed Description of the Invention]

[0001]

[Technical Field to which the Invention Belongs]

The present invention relates to an aqueous emulsion having high viscosity and good adhesiveness to wood and having good water resistance, and to an adhesive for wood that comprises the aqueous emulsion.

[0002]

[Prior Art]

Heretofore, polyvinyl alcohol (hereinafter this may be abbreviated to PVA) is widely used as a protective colloid in emulsion polymerization of an ethylenic unsaturated monomer, especially a vinyl ester monomer such as typically vinyl acetate. Vinyl ester-based aqueous emulsions obtained through emulsion polymerization with PVA serving as a protective colloid have many applications in various fields of adhesives for paper products, wood products, plastics, etc., binders for dip-coated papers, non-woven fabrics, etc., as well as admixtures, jointing agents, coating compositions, paper processing agents, fiber processing agents, etc. Controlling the degree of saponification of PVA therein makes it possible to change the physical properties of such aqueous emulsions, some of which will have low viscosity just like Newtonian fluid, and will be relatively highly resistant to water, while some others will have high viscosity relatively

independently of ambient temperatures. Depending on such their properties, aqueous emulsions containing PVA have many applications in various fields. For adhesives for wood, emulsions having higher viscosity are preferred, and vinyl ester-based aqueous emulsions comprising a protective colloid of partially-saponified PVA are widely used. Vinyl ester-based aqueous emulsions comprising a protective colloid of partially-saponified PVA have good low-temperature stability, and those having high viscosity are easy to obtain, but the emulsions have a problem in that their water resistance is not good. On the other hand, vinyl ester-based emulsions comprising a protective colloid of completely saponified PVA have good water resistance, but have a problem in that their low-temperature stability is not good. Given that situation, a vinyl alcohol polymer containing ethylene units has been proposed (JP-A 11-21529, 11-21380, 10-226774), and its water resistance and low-temperature storage stability have been greatly improved. At present, however, the viscosity of the emulsion obtained is generally lower than that of the emulsion comprising a protective colloid of partially-saponified PVA, and is therefore unsatisfactory for adhesives for wood.

[0003]

[Problems that the Invention is to Solve]

Given that situation, an object of the invention is to provide an aqueous emulsion having good low-temperature

stability and water resistance and having high viscosity, and to provide an adhesive for wood that comprises the aqueous emulsion.

[0004]

[Means for Solving the Problems]

We, the present inventors have assiduously studied so as to develop an aqueous emulsion having the above-mentioned preferable properties and an adhesive for wood, and, as a result, have found that an aqueous emulsion which comprises, as the dispersoid, a polymer having vinyl ester monomer units, and, as the dispersant, a composition comprising a vinyl alcohol polymer (A) having an ethylene unit content of from 0.5 to 10 mol% and a degree of saponification (X) of at least 95 mol%, and a vinyl alcohol polymer (B) having a degree of saponification (Y) of from 75 to 95 mol%, and satisfying $X - Y \geq 0.5$ mol% can satisfy the above-mentioned object. We have further found that an adhesive for wood that comprises the aqueous emulsion satisfies the above-mentioned object, and have completed the present invention.

[0005]

[Mode for Carrying out the Invention]

A method for producing the vinyl alcohol polymer (A) having an ethylene unit content of from 0.5 to 10 mol% and a degree of saponification of at least 95 mol% is not specifically defined, and the polymer may be obtained in any known method

of saponifying a copolymer of vinyl ester and ethylene. The vinyl alcohol polymer (B) having a degree of saponification of from 75 to 95 mol% may also be obtained in any known method.

[0006]

The vinyl ester includes vinyl formate, vinyl acetate, vinyl propionate, vinyl pivalate, etc. In general, vinyl acetate is preferred.

[0007]

Not detracting from the effect of the invention, (A) and (B) each may be copolymerized with any copolymerizable ethylenic unsaturated monomer. The ethylenic unsaturated monomer includes, for example, acrylic acid, methacrylic acid, fumaric acid, maleic acid (anhydride), itaconic acid, acrylonitrile, methacrylonitrile, acrylamide, methacrylamide, trimethyl(3-acrylamido-3-dimethylpropyl)ammonium chloride, acrylamido-2-methylpropanesulfonic acid and its sodium salt, ethyl vinyl ether, butyl vinyl ether, N-vinylpyrrolidone, vinyl chloride, vinyl bromide, vinyl fluoride, vinylidene chloride, vinylidene fluoride, tetrafluoroethylene, sodium vinylsulfonate, sodium allylsulfonate, and N-vinylamides such as N-vinylpyrrolidone, N-vinylformamide, N-vinylacetamide, etc. In addition, also usable herein are terminal-modified polymers that are obtained by polymerizing a vinyl ester monomer such as vinyl acetate in the presence of a thiol compound such as thiolacetic acid or mercaptopropionic acid

followed by saponifying the resulting polymer.

[0008]

The degree of saponification of the vinyl alcohol polymer (A) having an ethylene unit content of from 0.5 to 10 mol% and a degree of saponification of at least 95 mol% must be at least 95 mol%, but preferably at least 96 mol%, more preferably at least 97 mol%. When the degree of saponification is smaller than 95 mol%, then the water resistance of the aqueous emulsion obtained may lower. The degree of polymerization of the vinyl alcohol polymer is not specifically defined, but is generally from 100 to 8000, preferably from 300 to 3000. If the degree of polymerization thereof is smaller than 100, then the vinyl alcohol polymer could not serve as a protective colloid; but if larger than 8000, then the industrial production of the vinyl alcohol polymer of the type may be problematic. It is a matter of importance that the polymer has an ethylene content of from 0.5 to 10 mol%. If the content is smaller than 0.5 mol%, then the water resistance of the polymer emulsion may be poor; but if larger than 10 mol%, then the solubility in water of the vinyl alcohol polymer, which is intrinsic to the polymer, may lower.

[0009]

The degree of saponification of the vinyl alcohol polymer (B) having a degree of saponification of from 75 to 95 mol% falls preferably between 78 and 95 mol%, but more preferably

between 83 and 93 mol%, most preferably between 85 and 92 mol%. If the degree of saponification is smaller than 83 mol%, then the water resistance of the aqueous emulsion obtained may lower. If the degree of saponification is larger than 95 mol%, then the viscosity of the aqueous emulsion obtained may lower. The degree of polymerization of the vinyl alcohol polymer (B) is not specifically defined, but generally falls between 100 and 8000, more preferably between 300 and 3000. If the degree of polymerization is smaller than 100, then the vinyl alcohol polymer could not serve as a protective colloid; but if larger than 8000, then the industrial production of the vinyl alcohol polymer may be problematic. It is a matter of importance that the degree of saponification (X) of the vinyl alcohol polymer (A) and the degree of saponification (Y) of the vinyl alcohol polymer (B) satisfy $X - Y \geq 0.5\%$. Satisfying the condition, the aqueous emulsion composition obtained may have high viscosity and good water resistance. Preferably, $X - Y \geq 3$ mol%; more preferably $X - Y \geq 5$ mol%; most preferably $X - Y \geq 8$ mol%.

[0010]

The ratio of the vinyl alcohol polymers (A) to (B) for use in the invention must fall between 9.9/0.1 and 5/5, but preferably between 9.85/0.15 and 6/4, more preferably between 9.8/0.2 and 7/3. If the ratio of (A)/(B) is larger than 9.9/0.1, then the viscosity of the emulsion obtained may be low. If

the ratio of (A)/(B) is smaller than 5/5, then the water resistance of the emulsion obtained may lower.

[0011]

The vinyl ester monomer to constitute the dispersoid in the aqueous emulsion of the invention include vinyl formate, vinyl acetate, vinyl propionate, vinyl pivalate, etc. In general, vinyl acetate is preferred.

[0012]

Not detracting from the effect of the invention, the dispersoid may be copolymerized with any copolymerizable ethylenic unsaturated monomer. At least one monomer unit selected from ethylenic unsaturated monomers and dienic monomers includes olefins such as ethylene, propylene, isobutylene, etc.; halogeno-olefins such as vinyl chloride, vinyl fluoride, vinylidene chloride, vinylidene fluoride, etc.; vinyl esters such as vinyl formate, vinyl acetate, vinyl propionate, vinyl versatate, etc.; acrylic acid, methacrylic acid; acrylates such as methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, dodecyl acrylate, 2-hydroxyethyl acrylate, etc.; methacrylates such as methyl methacrylate, ethyl methacrylate, butyl methacrylate, 2-ethylhexyl methacrylate, dodecyl methacrylate, 2-hydroxyethyl methacrylate, etc.; dimethylaminoethyl acrylate, dimethylaminoethyl methacrylate and their quaternary derivatives; as well as acrylamide monomers such

as acrylamide, methacrylamide, N-methylolacrylamide,
 N,N-dimethylacrylamide, acrylamido-2-methylpropanesulfonic
 acid and its sodium salt, etc.; styrene monomers such as styrene,
 α -styrene, p-styrenesulfonic acid and its sodium and potassium
 salts; and other monomers such as N-vinylpyrrolidone, etc.;
 and dienic monomers such as butadiene, isoprene, chloroprene,
 etc.; further as well as polyfunctional monomers such as
 divinylbenzene, tetraallyloxyethane,
 N,N'-methylenebis-acrylamide,
 2,2'-bis(4-acryloxypolyethoxyphenyl)propane, 1,3-butylene
 glycol diacrylate, 1,5-pentanediol diacrylate,
 neopentylglycol diacrylate, 1,6-hexanediol diacrylate,
 diethylene glycol diacrylate, triethylene glycol diacrylate,
 tetraethylene glycol diacrylate, polyethylene glycol
 diacrylate, polypropylene glycol diacrylate, pentaerythritol
 triacrylate, trimethylolpropane triacrylate, pentaerythritol
 tetraacrylate, allyl methacrylate, 1,4-butanediol diacrylate,
 ethylene glycol dimethacrylate, 1,3-butylene glycol
 dimethacrylate, neopentylglycol dimethacrylate,
 1,6-hexanediol dimethacrylate, diethylene glycol
 dimethacrylate, triethylene glycol dimethacrylate,
 polyethylene glycol dimethacrylate, dipropylene glycol
 dimethacrylate, polypropylene glycol dimethacrylate,
 trimethylolethane trimethacrylate, trimethylolpropane
 trimethacrylate,

2,2-bis(4-methacryloxypolyethoxyphenyl)propane, aluminium methacrylate, zinc methacrylate, calcium methacrylate, magnesium methacrylate, N,N'-m-phenylenebismaleimide, diallyl phthalate, triallyl cyanurate, triallyl isocyanurate, triallyl trimellitate, diallyl chlorendate, ethylene glycol diglycidyl ether acrylate, etc. One or more of these may be used herein either singly or as combined. As the monomer copolymerizable with vinyl esters, ethylene is preferred.

[0013]

The method for producing the aqueous emulsion for use in the invention is not specifically defined. For example, an aqueous solution of vinyl alcohol polymers (A) and (B) is used as a dispersant, and a vinyl ester monomer is added to it at a time or continuously, and a polymerization initiator, for example, an azo-type polymerization initiator or a peroxide-type polymerization initiator such as hydrogen peroxide, ammonium persulfate or potassium persulfate is added to it, and the monomer is polymerized in a mode of emulsion polymerization.

[0014]

The total amount of the vinyl alcohol polymers (A) and (B) to be used is not specifically defined. Preferably, it is from 3 to 20 parts by weight, more preferably from 5 to 15 parts by weight, relative to 100 parts by weight of the vinyl ester monomer-containing polymer. If the amount used is

smaller than 3 parts by weight, then the polymerization stability may lower; but if larger than 20 parts by weight, then the storage stability of the emulsion obtained may lower.

[0015]

Regarding the aqueous emulsion and the adhesive for wood of the invention, the aqueous emulsion obtained according to the method as above may be directly used as it is, but if desired, it may be mixed with any known emulsion not detracting from the effect of the invention. For the dispersant in the aqueous emulsion of the invention, used are the above-mentioned vinyl alcohol polymers (A) and (B), but if desired, they may be combined with any known anionic, nonionic or cationic surfactant or hydroxyethyl cellulose, and may be further combined with any other vinyl alcohol polymer except the vinyl alcohol polymers (A) and (B) not detracting from the object of the invention. These additives may be added to the aqueous emulsion as later additives.

[0016]

The aqueous emulsion and the adhesive for wood of the invention have high viscosity, good water resistance and good low-temperature stability, and are favorably used in various fields of wood-processing adhesives for flush panels, wood laminates, butt-welded wood plates, plywood products, secondary worked plywood products (for jointing them), other ordinary wood products, etc.; adhesives for others; binders

for dip-coated papers and non-woven fabrics; as well as admixtures, jointing agents, coating compositions, paper processing agents, fiber processing agents, etc.

[0017]

[Examples]

The invention is described in more detail with reference to the following Examples and Comparative Examples. Unless otherwise specifically indicated, "parts" and "%" in the following Examples and Comparative Examples are all by weight. The emulsions prepared were tested for water resistance and storage stability, according to the methods mentioned below.

[0018]

(Emulsion Evaluation)

(1) Emulsion Viscosity:

Using a BH-type viscometer (by Tokimec), the viscosity of the aqueous emulsion and the aqueous emulsion composition obtained was measured at 30°C and at 20 rpm.

(2) Adhesiveness to Wood:

The aqueous emulsion composition obtained is applied to a birch plate (straight-grained) in an amount of 50 g/m², and the two plates are stuck to each other and compressed under a load of 7 kg/m² for 16 hours. Next, the pressure is removed, and the bonded sample is aged at 20°C and 65% RH for 5 days. With that, its compression shear strength is measured (ordinary state adhesiveness). After thus aged, the sample

is dipped in hot water at 60°C for 3 hours, and, while wetted, its compression shear strength is measured (hot water-resistant adhesiveness).

Low-Temperature Stability:

The emulsion is left at 0°C, and after 14 days, its viscosity change is observed.

O: Little change found.

Δ: Some viscosity increase found.

x: Viscosity increase and gelling found.

[0019]

Example 1:

300 g of ion-exchanged water, 24.7 g of PVA-1 (degree of polymerization 1000; degree of saponification 99.2 mol%; ethylene unit content 6 mol%), and 1.3 g of PVA-2 (degree of polymerization 1700; degree of saponification 88 mol%; Kuraray's PVA-217) were put into a 1-liter glass polymerization reactor equipped with a reflux condenser, a dropping funnel, a thermometer and a nitrogen inlet mouth (PVA-1/PVA-2 = 9.5/0.5), and completely dissolved at 95°C. Next, the aqueous PVA solution was cooled and purged with nitrogen, and then heated up to 60°C while stirred at 200 rpm, and thereafter 4.4 g of aqueous 10% solution of tartaric acid and 3 g of aqueous 5% hydrogen peroxide (in a ratio by mol of 0.015 to vinyl acetate) were added to it as a shot, and then 26 g of vinyl acetate was fed into it and its polymerization

was started. 30 minutes after the start of the polymerization, the termination of the initial polymerization was confirmed. 0.9 g of aqueous 10% tartaric acid solution and 3 g of aqueous 5% hydrogen peroxide were added to it as a shot, and then 234 g of vinyl acetate was continuously added to it, taking 2 hours, and the polymerization was thus finished. Then, this was cooled. Next, this was filtered through a 60-mesh stainless metal gauze. As a result, a polyvinyl acetate emulsion having a solid content (TSC) of 48.3% was obtained. To 100 parts by weight of the emulsion, added was 5 parts of dibutyl phthalate. The physical properties of the emulsion (Em-1) were measured according to the methods mentioned above. The results are shown in Table 1.

[0020]

Example 2:

Em-2 was obtained in the same manner as in Example 1, for which, however, the ratio of PVA-1/PVA-2 was changed from 9.5/0.5 to 9/1. The physical properties of the emulsion are shown in Table 1.

[0021]

Example 3:

Em-3 was obtained in the same manner as in Example 1, for which, however, the ratio of PVA-1/PVA-2 was changed from 9.5/0.5 to 8/2. The physical properties of the emulsion are shown in Table 1.

[0022]

Example 4:

Em-4 was obtained in the same manner as in Example 2, for which, however, PVA-3 (degree of polymerization 2400; degree of saponification 88 mol%; Kuraray's PVA-224) was used in place of PVA-2. The physical properties of the emulsion are shown in Table 1.

[0023]

Example 5:

Em-5 was obtained in the same manner as in Example 2, for which, however, PVA-4 (degree of polymerization 3500; degree of saponification 88 mol%; Kuraray's PVA-235) was used in place of PVA-2. The physical properties of the emulsion are shown in Table 1.

[0024]

Example 6:

Em-6 was obtained in the same manner as in Example 2, for which, however, PVA-5 (degree of polymerization 2000; degree of saponification 80 mol%; Kuraray's PVA-420) was used in place of PVA-2. The physical properties of the emulsion are shown in Table 1.

[0025]

Comparative Example 1:

Em-7 was obtained in the same manner as in Example 1, for which, however, PVA-2 was not used. The physical

properties of the emulsion are shown in Table 1.

[0026]

Comparative Example 2:

Em-8 was obtained in the same manner as in Example 2, for which, however, PVA-6 (degree of polymerization 1700; degree of saponification 98.5 mol%; Kuraray's PVA-117) was used in place of PVA-2. The physical properties of the emulsion are shown in Table 1.

Comparative Example 3:

Em-9 was obtained in the same manner as in Example 1, for which, however, PVA-1 was not used. The physical properties of the emulsion are shown in Table 1.

[0027]

Example 7:

300 g of ion-exchanged water, 17.6 g of PVA-7 (degree of polymerization 1700; degree of saponification 98.2 mol%; ethylene unit content 4 mol%), and 1.9 g of PVA-2 were put into a 1-liter glass polymerization reactor equipped with a reflux condenser, a dropping funnel, a thermometer and a nitrogen inlet mouth (PVA-7/PVA-2 = 9/1), and completely dissolved at 95°C. Next, the aqueous PVA solution was cooled and purged with nitrogen, and then heated up to 60°C while stirred at 200 rpm, and thereafter 4.4 g of aqueous 10% solution of tartaric acid and 3 g of aqueous 5% hydrogen peroxide (in a ratio by mol of 0.015 to vinyl acetate) were added to it as a shot, and

then 26 g of vinyl acetate was fed into it and its polymerization was started. 30 minutes after the start of the polymerization, the termination of the initial polymerization was confirmed. 0.9 g of aqueous 10% tartaric acid solution and 3 g of aqueous 5% hydrogen peroxide were added to it as a shot, and then 234 g of vinyl acetate was continuously added to it, taking 2 hours, and the polymerization was thus finished. Then, this was cooled. Next, this was filtered through a 60-mesh stainless metal gauze. As a result, a polyvinyl acetate emulsion having a solid content of 47.2% was obtained. To 100 parts by weight of the emulsion, added was 5 parts of dibutyl phthalate. The physical properties of the emulsion (Em-10) are shown in Table 1.

[0028]

Comparative Example 4:

Em-11 was obtained in the same manner as in Example 7, for which, however, PVA-7 was used in place of using PVA-2 (that is, PVA-7 was used alone). The physical properties of the emulsion are shown in Table 1.

[0029]

[Table 1]

	Dispersant	Emulsion	TSC (%)	Viscosity (mPa·s)	Adhesiveness (kg/cm ²)		Low-Temperature Stability
					ordinary state	hot-water resistance	
Example 1	PVA-1/PVA-2 = 9.5/5	Em-1	48.3	12000	120	35	○
Example 2	PVA-1/PVA-2 = 9/1	Em-2	48.2	20000	125	30	○
Example 3	PVA-1/PVA-3 = 8/2	Em-3	48.3	70000	130	31	○
Example 4	PVA-1/PVA-3 = 9/1	Em-4	48.4	30000	125	35	○
Example 5	PVA-1/PVA-4 = 9/1	Em-5	48.0	45000	180	34	○
Example 6	PVA-1/PVA-5 = 9/1	Em-6	48.6	23000	120	29	○
Comparative Example 1	PVA-1 alone	Em-7	48.4	5000	100	28	○
Comparative Example 2	PVA-1/PVA-6 = 9/1	Em-8	48.3	4000	95	8	×
Comparative Example 3	PVA-2 alone	Em-9	48.3	21000	110	0	○
Example 7	PVA-7/PVA-2 = 9/1	Em-10	47.3	18000	180	32	○
Comparative Example 4	PVA-7 alone	Em-11	47.2	7000	110	20	○

[0030]

PVA-1: degree of polymerization 1000, degree of saponification 99.2 mol%, ethylene unit content 6 mol%

PVA-2: degree of polymerization 1700, degree of saponification 88 mol%, Kuraray's PVA-217

PVA-3: degree of polymerization 2400, degree of saponification 88 mol%, Kuraray's PVA-224

PVA-4: degree of polymerization 3500, degree of saponification 88 mol%, Kuraray's PVA-235

PVA-5: degree of polymerization 2000, degree of saponification 80 mol%, Kuraray's PVA-420

PVA-6: degree of polymerization 1700, degree of saponification 98.5 mol%, Kuraray's PVA-117

PVA-7: degree of polymerization 1700, degree of saponification 98.1 mol%, ethylene unit content 4 mol%

[0031]

[Advantage of the Invention]

The aqueous emulsion and the adhesive for wood of the invention have high viscosity, good water resistance and good adhesiveness to wood, and are favorably used in various fields of wood-processing adhesives for flush panels, wood laminates, butt-welded wood plates, plywood products, secondary worked plywood products (for jointing them), other ordinary wood products, etc.; adhesives for others; binders for dip-coated papers and non-woven fabrics; as well as admixtures, jointing

agents, coating compositions, paper processing agents, fiber processing agents, etc.